ORIENTED TRANSFORMATION OF MAGNESITE

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Plate XI

ABSTRACT. The transformation of magnesite into periclase under heat treatment has been studied by single crystal X-ray diffraction method. It was observed that a single crystal of magnesite, when heated to about 450°C, transformed into a single crystal of periclase with orientational relationships between the two phases. One of the triad axes of rhombohedral crystal of magnesite became parallel to one of the triad axes of cubic crystal of periclase with three diad axes of both the phases being interchanged.

INTRODUCTION

Magnesite ($MgCO_3$) falls in the calcite group of minerals. Though no single crystal structure analysis of this particular mineral has been done, its difference from that of calcite is only in its cell dimensions, the positions of calcium ions being replaced by magnesium ions in magnesite. A pure magnesite should have a chemical formula like $MgCO_3$; but in nature a slight amount of Mg^{++} is always replaced by other divalent ions such as Fe^{++}, Mn^{++}, Ca^{++} etc. Thermal decomposition of magnesite had been studied by different workers (Cuthbert and Rowland, 1947; Weiden, 1954) and in the d.t.a. curve for magnesite an endothermic peak at around 650°C and a small exothermic peak at a slightly higher temperature were observed. The endothermic peak was due to the decomposition of magnesite into periclase (MgO) and CO_2; the exothermic peak was explained as due to the crystallisation of periclase. Kulp, Kent and Kerr (1951) observed that the peak temperature for endothermic reaction varied within a range of 660° to 690°C. Beck (1950) had ascribed the inflection on the downward sweep in the d.t.a. curve, after the main endothermic peak, to the formation of an intermediate carbonate such as $MgO.MgCO_3$. But his X-ray study did not provide any conclusive evidence. Cramer and Bachman (1955) studied the transformation of $MgCO_3$ under various pressures of CO_2. Their observation under the electron microscope showed the following : The shape of magnesite grains remained unchanged during the decomposition. MgO was first formed on the outer side of $MgCO_3$ grains as a fluffy layer of small crystallites. With increasing CO_2 pressure, the size of MgO crystallites increased and the velocity of decomposition decreased. The thermal transformation of siderite ($FeCO_3$), a mineral belonging to the same structural group, was studied by Bernal, Dasgupta and Mackay (1959) and Dasgupta

(1960) by X-ray diffraction method. Cleavage rhombohedron of siderite was sealed in a tube under vacuum and heated to about 550°C. After rapide ooling it was observed that the crystal, without changing its shape, became highly magnetic and the X-ray examination of the same crystal revealed the presence of oriented intergrowths of FeO and Fe_3O_4. However, upto the present time no work on the transformation of magnesite by single crystal X-ray diffraction method has come to the author's notice. The present work was, therefore, intended for finding out if magnesite would also transform into periclase with orientational relationships between the two phases.

EXPERIMENTAL

Beautiful milky white single crystals of rhombohedral shape were separated from sample (Ind. Mus. Reg. No. 8677, found at Dhoba and Delwaldhar, Almora Dt., Uttar Pradesh). The sample as a whole, when examined by X-ray powder diffraction method, proved to be mainly magnesite with minor amount of dolomite and traces of talc. However, single crystals, separated from that sample, did not contain dolomite or talc. Rotation photograph of one such crystal, taken along the two-fold axis of the rhombohedral crystal in a 3 cm. radius cylindrical camera with Ni-filtered Cu-radiation, is shown in Fig. 1. Similar crystals were heated in a covered porcelain crucible at about 450°C for five hours and then cooled down to room temperature. It was observed that the crystals decrepitated and had broken down into small fragments. The colour of the small fragments turned slightly pinkish but the rhombohedral shape was still maintained in those small fragments. A 30° oscillation photograph of one such crystal along the same axis as before was taken in the same camera with similar radiation (Fig. 2). It was seen that the crystal was partly transformed into periclase. The sharp spots in Fig. 2 were due to untransformed magnesite, while the powder diffraction arcs showing definite preferred orientation were due to periclase. Measurement of periodicity from the fibre pattern due to periclase showed that the direction of preferred orientation coincided with a two-fold axial direction of the cubic crystal of periclase. It has been already stated that the crystals of magnesite heated to 450°C turned slightly pinkish. But when such crystals were powdered, it was observed that the inner portions of the crystals were still milky white, indicating that the surface of the crystal was affected first during the transformation. This seems to be in agreement with Cremer and Bachman's (1955) observation. Powder diffraction photograph of crystals of magnesite heated to 600°C for five hours showed complete conversion of magnesite into periclase with a slight change in the degree of crystallisation.

DISCUSSIONS

The orientational relationship, which was observed during the transformation of magnesite to periclase, can be explained from structural point of view. Magnesite, which has a face-centred rhombohedral structure, can be very well

Fig 1 Fig. 2

Fig. 1. Rotation photograph of single crystal of magnesite taken along a diad axis of the rhombohedral crystal with Ni-filtered Curadiation

Fig. 2. Rotation photograph of single crystal of magnesite heated to 450 C. taken along the same direction with same radiation.

compared to a distorted NaCl structure. If the $MgCO_3$ structure is considered along a threefold axis of the rhombohedral crystal, it can be seen that the CO_3 ions are arranged in cubic closed-packed (ABCABCABCA...) layers with Mg^{++} ions in octahedral positions in between layers. The oblate shape of the CO_3^{--} ions makes the crystal to be rhombohedral instead of being cubic. Periclase, on the other hand, has a simple NaCl structure. The arrangements of CO_3 and O^{--} along the three-fold axis of magnesite and periclase are shown in Fig. 3.

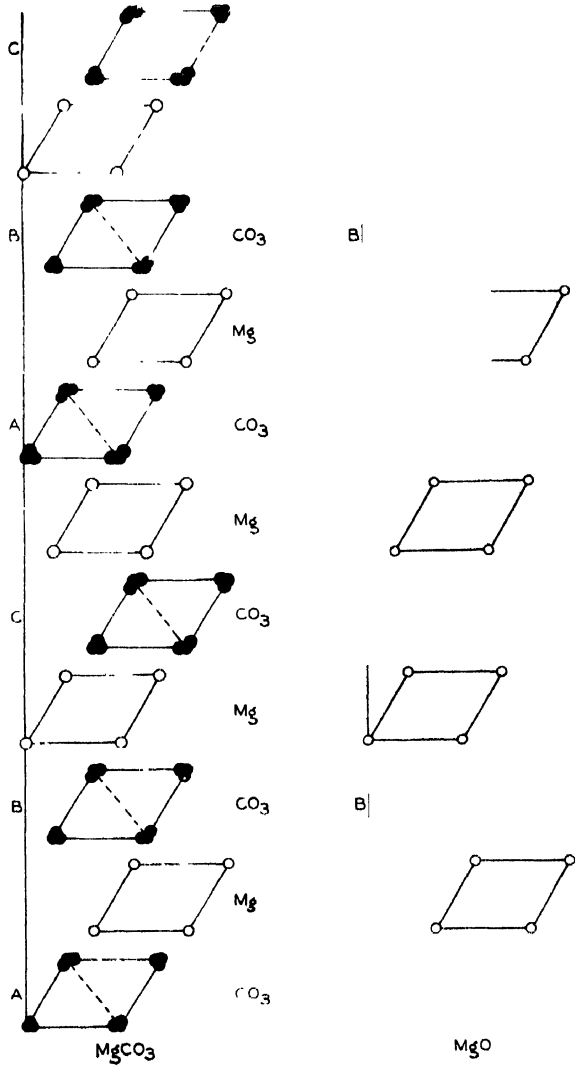

Fig. 3. Arrangements of CO_3 and O layers along three-fold axis in Magnesite and Periclase Mg layers are placed in octahedral position in between CO_3 and O layers.

To arrive at the structure of periclase from that of magnesite, all one has to do is to press the structure along the three-fold axis till the edges meeting that axis make angles equal to 90° to each other. So, when magnesite is heated, CO_2

begins to come out from the CO_3^{--} layers as a result of which a strain is produced along the three-fold axis. With the complete expulsion of CO_2, the rhombohedral cell changes into a cubic cell of periclase. Thus, a three-fold axis of the rhombohedral magnesite crystal becomes a three-fold axis of the cubic periclase crystal, the three diad axes of both the phases being interchanged with each other. The effect of strain in changing the rhombohedral cell into a cubic cell is very much evident from the X-ray photograph due to periclase.

It may be pointed out here that in the case of $FeCO_3$ a similar sort of oriented decarbonation occured (Bernal, Dasgupta and Mackay, 1959; Dasgupta, 1960) and attention was drawn to the difficulty of reconciling this with the fact that two-thirds of the oxygen was lost during the decomposition. Ball and Taylor (1961) suggested that this difficulty could be removed if an inhomogeneous mechanism of transformation is considered in this case. The fact that the surface of the magnesite crystal was affected first during the transformation may be an indication for an inhomogeneous mechansim. In that case one is tempted to think that there are acceptor and donor regions in the magnesite crystals and the migrations of ions from these regions may take place in the following way :

Acceptor regions : $MgCO_3$..... $3M_gO$

$\uparrow 2Mg^{++}$ $\downarrow C^{++++}$

Donor regions : $2MgCO_3$ ..... $3CO_2$

However, it will be very much premature to describe the mechanism of transformation like this unless a complete study is made with other minerals of the calcite group.

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